

# A NEW GENERATION OF OXYNITRIDE GLASSES CONTAINING FLUORINE

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**Abstract:** Oxynitride glasses are found as grain boundary phases in silicon nitride ceramics. They are effectively alumino-silicate glasses in which nitrogen substitutes for oxygen in the glass network, and this causes increases in glass transition and softening temperatures, viscosities (by two to three orders of magnitude), elastic moduli and microhardness. Calcium silicate-based glasses containing fluorine are known to have useful characteristics as potential bioactive materials. Therefore, the combination of both nitrogen and fluorine additions to these glasses may give useful glasses or glass-ceramics with enhanced mechanical stability for use in biomedical applications. This paper reports glass formation and evaluation of glass thermal properties in the Ca-Si-Al-O-N-F system. Within the previously defined Ca-Si-Al-O-N glass forming region at 20 eq.% N, homogeneous, dense glasses are formed. However, addition of fluorine affects glass formation and the reactivity of glass melts. This can lead to fluorine loss as SiF<sub>4</sub>, and also nitrogen loss, leading to bubble formation and porous glasses. The compositional limits for both dense and porous glass formation at 20 eq.% N and 5 eq.% F have been mapped. At high fluorine contents under conditions when Ca-F bonding is favoured, CaF<sub>2</sub> crystals precipitate in the glass. The role of the different cations on glass formation in these oxyfluoro-nitride glasses is discussed.

**Keywords:** Ca-SiAlON, Oxynitride, Fluorine, Glass Formation, Thermal Properties

## 1. INTRODUCTION

Oxynitride glasses form in silicate and alumino-silicate systems when a nitrogen containing compound such as Si<sub>3</sub>N<sub>4</sub> dissolves to form a M-Si-O-N or M-Si-Al-O-N liquid at ~1600-1700°C and cools to form a glass (M is usually a di-valent [Mg, Ca] or tri-valent [Y, Ln] cation. Jack was the first to report glass formation in oxynitride glasses [1]. Early work on the correlations between nitrogen incorporation into oxynitride glasses and changes in their physical properties was reported by Loehman [2-4]. The first systematic studies on the effect of replacing oxygen by nitrogen in oxynitride glasses, with fixed cation compositions, on properties were reported by Drew et al. [5, 6] and Hampshire et al. [7]. Glass forming regions for Mg-, Ca- and Y-Si-Al-O-N glasses were also mapped out. Glass forming regions of oxynitride glasses containing rare earth elements were investigated later [8-10].

The systematic substitution of oxygen by nitrogen [5-7] results in increases in the glass transition temperature, hardness, Young's modulus and fracture toughness of these glasses and decreases in the thermal expansion coefficient, due to the ability of nitrogen to

increase the cross-link density in the glass network. Also nitrogen lowers the melting temperature and increases the viscosity of the melt which enhances glass forming ability and subsequent stability [5-7, 9, 11, 12]. Al is known to expand the compositional range for glass formation in these systems, lower the melt temperature, increase nitrogen solubility and, in amounts of only a few atomic percent, suppress the phase separation observed in its absence [4, 10, 13].

Fluorine in silicate and alumino-silicate glasses acts as a powerful network disrupter which substitutes for bridging oxygen ions [14]. Fluorine reduces the glass transition temperature, viscosity and refractive index, aids crystallisation and increases the potential for phase separation [15]. The effect of fluorine addition on the structure of silicate or aluminosilicate glasses containing alkaline earth cations has been reported [14,16] and it has been shown that fluorine may bond to silicon as Si-F, to Al as Al-F, or to Ca as Ca-F. Fluorine loss (as SiF<sub>4</sub>) occurs under conditions where formation of the Si-F bond is favoured. The bonding of fluorine to aluminum prevents fluorine loss from the glass melt and explains the reduction in the glass

transition temperature [14].

The aim of the current work was to explore a new generation of oxynitride glasses containing fluorine and to develop an initial understanding of the effects of composition on glass formation, structure and thermal properties. For successful production of dense glasses in the Ca-Si-Al-O-N-F system, fluorine loss needs to be suppressed by means of careful design of chemical composition.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Preparation of Ca-Si-Al-O-N-F Glasses

The extent of the glass forming regions in various M-Si-Al-O-N systems (M = Ca, Mg, Y, etc.) has been studied previously [5-7, 11, 13, 17] and represented using the Jänecke prism [5-7, 11, 17] with compositions expressed in equivalent percent (eq.%) of cations and anions instead of atoms or gram-atoms. One equivalent of any element always reacts with one equivalent of any other element or species. For a system containing three types of cations, A, B and C with valencies of  $v_A$ ,  $v_B$ , and  $v_C$ , respectively, then:

Equivalent concentration of

$$A = (v_A [A]) / (v_A [A] + v_B [B] + v_C [C]),$$

where [A], [B] and [C] are, respectively, the atomic concentrations of A, B and C, in this case,  $\text{Si}^{\text{IV}}$ ,  $\text{Al}^{\text{III}}$  and  $\text{Ca}^{\text{II}}$ .

If the system also contains three types of anions, D, E and F with valencies  $v_D$ ,  $v_E$  and  $v_F$ , respectively, then:

Equivalent concentration of

$$D = (v_D [D]) / (v_D [D] + v_E [E] + v_F [F]),$$

where [D], [E] and [F] are, respectively, the atomic concentrations of D, E and F, i.e.  $\text{O}^{\text{II}}$ ,  $\text{N}^{\text{III}}$  and  $\text{F}^{\text{I}}$ .

To find the glass forming region in the Ca-Si-Al-O-N-F system, the previously reported glass forming region [7] of the Ca-Si-Al-O-N system at 20 eq.% nitrogen at 1700 °C was used as the basis for further exploration with 5 eq.% F. Compositions within and outside this region were studied to evaluate the effects on glass formation at 1650 °C of adding fluorine.

Changes in Ca:Al:Si cation ratios were made systematically in order to study the complete glass forming region at the fixed O:N:F ratio.

Glasses were prepared from mixtures of silicon nitride powder (UBE) and  $\text{CaF}_2$  (Aldrich), together with high purity (99.9%)  $\text{SiO}_2$  (Fluka Chemika),  $\text{Al}_2\text{O}_3$  (Sumitomo),  $\text{CaO}$  (Fisher) to give the required chemical composition in eq.% cations/anions.

Powder samples of total weight 10g were mixed using a magnetic stirrer in 50 ml isopropanol which was then evaporated using a hot plate. Compacts of 10 mm height and 20 mm diameter were pressed under 20 tonnes pressure. These were melted in a boron nitride lined graphite crucible under 0.1 MPa nitrogen at 1650°C for 1 h in a vertical  $\text{Al}_2\text{O}_3$  tube furnace, after which the crucible was withdrawn rapidly from the hot zone to ambient temperature. The cooling rate was estimated to be  $\sim 100^\circ\text{C}/\text{min}$ . The solid glass sample was removed and cleaned using an ultrasonic bath prior to further analysis.

### 2.2. Characterisation of Glasses

X-ray diffraction analysis was used to determine if the samples were amorphous or crystalline and to identify the crystalline phases. Differential thermal analysis was carried out using a Stanton-Redcroft STA 1640 instrument. 50 mg of glass powder was heated at  $10^\circ\text{C}/\text{min}$  under 0.1 MPa nitrogen atmosphere. To find  $T_{\text{gonset}}$  and  $T_{\text{goffset}}$ , the first derivative was analysed and to find the  $T_g$ , the second derivative was analysed. Crystallisation and melting temperatures were obtained from the maxima in the peaks on the original DTA curve.

In order to study the crystallisation behaviour of glasses in oxyfluoronitride series, glasses were heat treated at nucleation temperature of ( $T_g+50^\circ\text{C}$ ) for 5 h followed by 10 h at  $T_c$ , the crystallisation temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. Glass Formation in the Ca-Si-Al-O-N-F System

Fig. 1 shows the 75 compositions which were investigated to find the glass forming region at 20 eq.% N and 5 eq.% F. The cation compositions, which were selected from the amorphous and crystalline regions of the original Ca-Si-Al-O-N

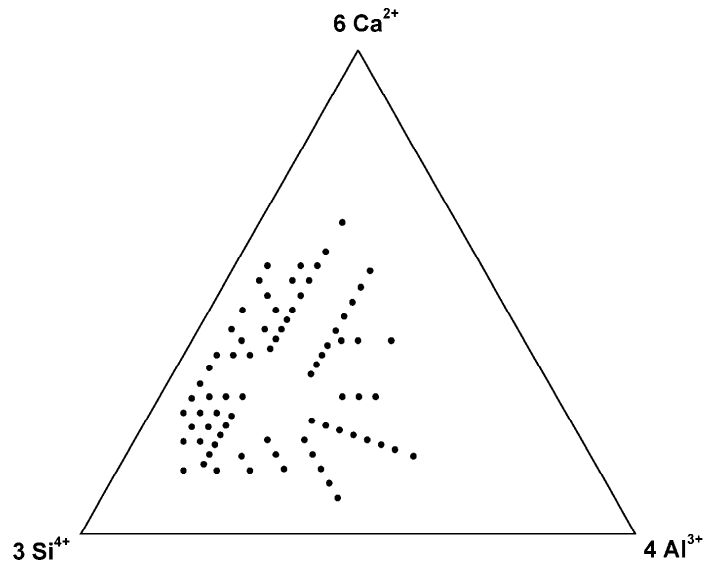


Fig. 1. Compositions studied (75) to investigate the glass forming region at 20 eq.% Nitrogen and 5 eq.% Fluorine in the Ca-Si-Al-O-N-F system.

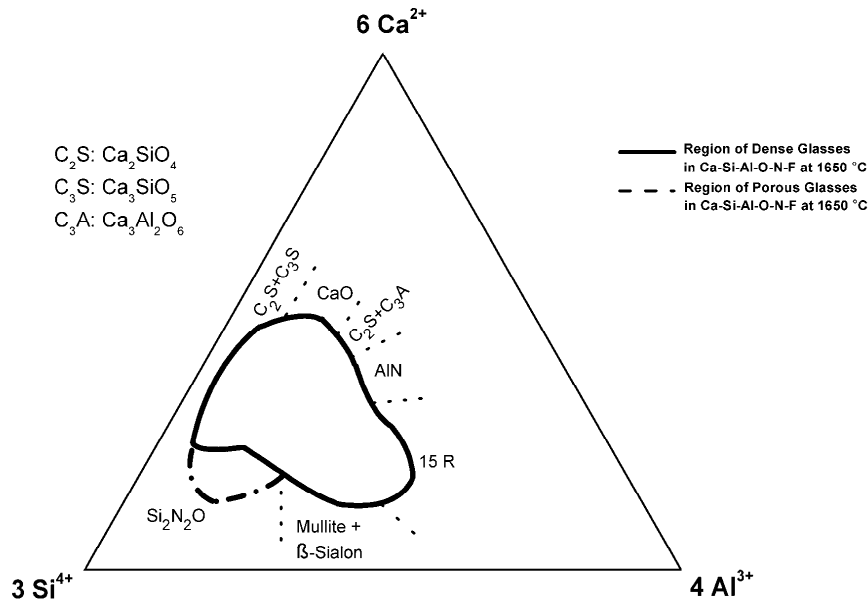


Fig. 2. The glass forming region at 1650°C found in the Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F and the adjacent crystalline regions.

diagram, were changed systematically by 2-3 eq.% for each attempt.

Fig. 2 shows the glass forming region found for the Ca-Si-Al-O-N-F system 20 eq.% N and 5 eq.% F at 1650°C based on the different compositions shown in Fig. 1. In the surrounding regions the different crystalline phases observed are also shown. All glasses were dense except for a region of Si-rich compositions where porous glasses were observed. In the porous glass area of

Fig. 2, there are bubbles on the surface in addition to the bubbles (pores) within the bulk of the glasses which is due to  $\text{SiF}_4$  loss. Formation of  $\text{SiF}_4$  is favored perhaps due to high Si:F ratios (>3) and low Al (6-15 eq.%) and Ca (13-25 eq.%) contents.

In some areas of this glass forming region inhomogeneous and phase separated glasses were found similar to other previously reported oxyfluoride and oxynitride glasses [14, 18, 19].

Different rules have been proposed to keep Al in 4-fold coordination in calcium aluminosilicate glasses, so combining with fluorine and preventing its loss [20, 21]. When Al:Si ratio is  $<1$ , Al is in 4-fold coordination and Al may enter the glass network as  $[\text{AlO}_4]^{5-}$  tetrahedra [20]. When Ca:Al ratio  $>1:2$  and Al:Si ratio  $<1:1$ , Al is thought to be in 4-fold coordination as Ca ions can charge balance  $[\text{AlO}_4]^{5-}$  tetrahedra [21]. When Al:Si ratio is  $>1$  or Ca:Al is  $<1:2$ , then some of the Al ions take up 6-fold coordination and so F tends to bond to Si which creates instability in the melt and loss of volatile  $\text{SiF}_4$  [21, 22]. Fluorine loss can be suppressed by incorporation of sufficient basic network modifying oxide which in this system is CaO [14]. When there is sufficient Ca to form non-bridging oxygens, Si-F bond formation is prevented and, hence, no loss of  $\text{SiF}_4$  can occur [23]. In addition, nitrogen increases the cross-linking in the network and, thus, can be bonded to either three Si atoms or only two [11] and still act as an effective bridging anion and therefore prevent formation of  $\text{SiF}_4$ .

In the case of Al, if Al:F = 1:1, then sufficient Al ions are present to satisfy the F ions present and form Al-F bonds. For 5 eq.% F, this requires 15 eq.% Al. Al-F bonds are favoured at Al  $> 15$

eq.%, unless Al:Si  $>1$  which leads to instability in the glass network and formation of Si-F bonds leading to possible  $\text{SiF}_4$  bubble formation, resulting in porous samples. When Al:Si  $\gg 1$ , glass formation becomes difficult and calcium fluoride ( $\text{CaF}_2$ ) is precipitated.

At  $< 15$  eq.% Al (greater Ca content), a large area of dense glasses is observed which is evidence of the formation of Ca-F bonds since there is insufficient Al to satisfy all the F as Al-F bonds. While the samples are not porous,  $\sim 3\%$  weight loss occurs in these glasses, which means that N or F loss is still inevitable. At low Al contents (3-4%), samples were bloated and large weight losses observed. This is mainly due to the shift of the cation composition towards the CaO-SiO<sub>2</sub> binary which does not show a tendency for glass formation. Al-free Ca-Si oxynitride glasses are phase separated and addition of a few weight percentage of  $\text{Al}_2\text{O}_3$  suppresses the phase separation in such systems [12].

Fig. 3 compares the glass forming region at 1650°C in the Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F (solid lines) with the glass forming region at 1700°C in the Ca-Si-Al-O-N system at 20 eq.% N (dotted line) [7]. The figure shows that, by addition of fluorine, the glass forming region has expanded towards more Ca-

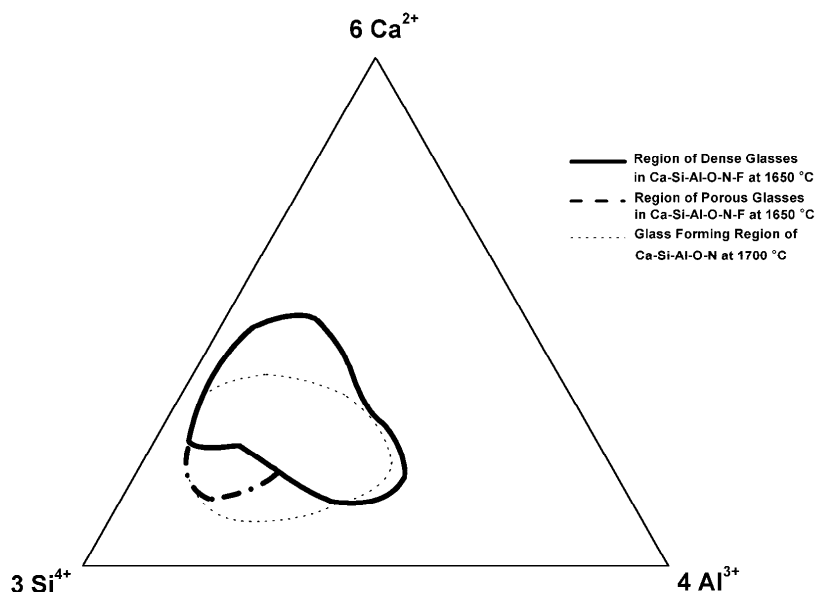


Fig. 3. Comparison of glass forming region at 1650°C in the Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F and glass forming region at 1700°C in the Ca-Si-Al-O-N system at 20 eq.% N [7].

rich compositions. The glass forming region for the Ca-Sialon system at 1700°C is smaller than the area determined for Ca-Si-Al-O-N-F glasses at 1650°C and so it is clear that fluorine has a significant effect in expanding the glass forming region.

For a better understanding of the role of fluorine on thermal properties of glasses, some glasses with different cation ratios in the Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F were selected. The melting points of these compositions were found from DTA analysis and compared with the liquidus temperatures of the same eq.% cation compositions found in the ternary of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system [24]. Fig. 4 compares the liquidus temperatures for these oxide and oxyfluoronitride compositions. It is obvious that the addition of both nitrogen and fluorine reduces the liquidus temperatures of the high silica and alumina compositions by 100-250°C. At high SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents, there is not too much difference in the area of glass formation in both the Ca-Si-Al-O-N and Ca-Si-Al-O-N-F systems. However, there is a large expansion of glass formation in Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F compared with the Ca-Si-Al-O-N system at 20 eq.% N, which is mainly due to the effect of nitrogen and fluorine together, as evidenced by the much lower

liquidus temperatures of about 800°C at higher Ca contents. In the Ca-Si-Al-O-N system, high calcium compositions in this region are not fully melted and contain solid crystalline phases at 1700°C. Therefore the role of fluorine is to reduce the liquidus temperature and it also decreases glass transition temperature (see later) which may allow an extension of the melting range and so enhance glass formation.

In relation to melting temperatures, it was observed that by the addition of a defined amount of CaF<sub>2</sub> to Ca-Si-Al-O-N glasses and then remelting of the batch, a dense transparent Ca-Si-Al-O-N-F glass can be obtained at a temperature of 1500°C.

Fig. 5 shows regions which specify the homogeneity and the colour of the obtained glasses in this system. Within the area outlined in bold, dense homogeneous or inhomogeneous glasses or samples with few bubbles on the surface were obtained while in the area outlined by a dashed line, porous homogenous glasses were obtained. Most of the glasses in this system are gray or black in colour. The homogeneity of glasses is not only a function of composition and purity but also the melting conditions such as temperature or cooling rate; nitrogen pressure and pouring are important factors in this regard. Glasses in this system are mainly opaque but in

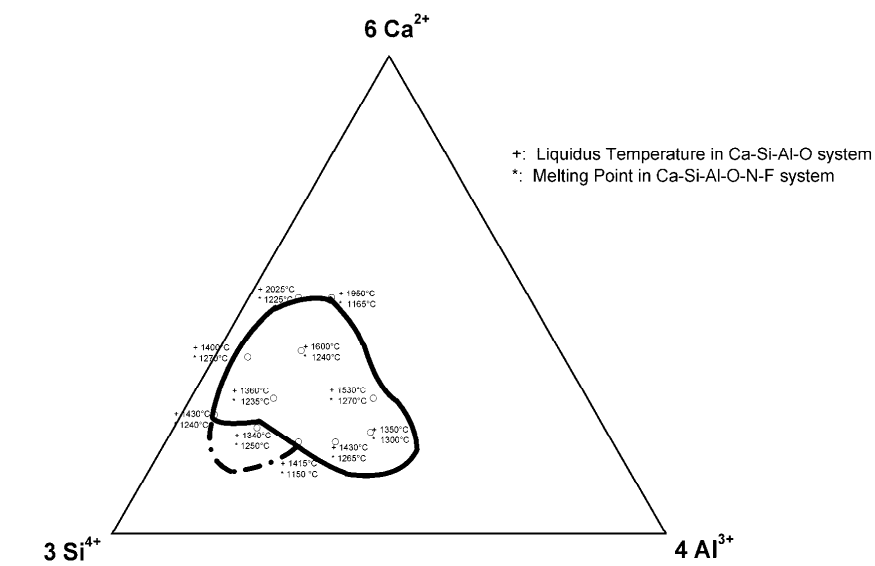


Fig. 4. Comparison of melting points of oxide and oxyfluoronitride compositions.

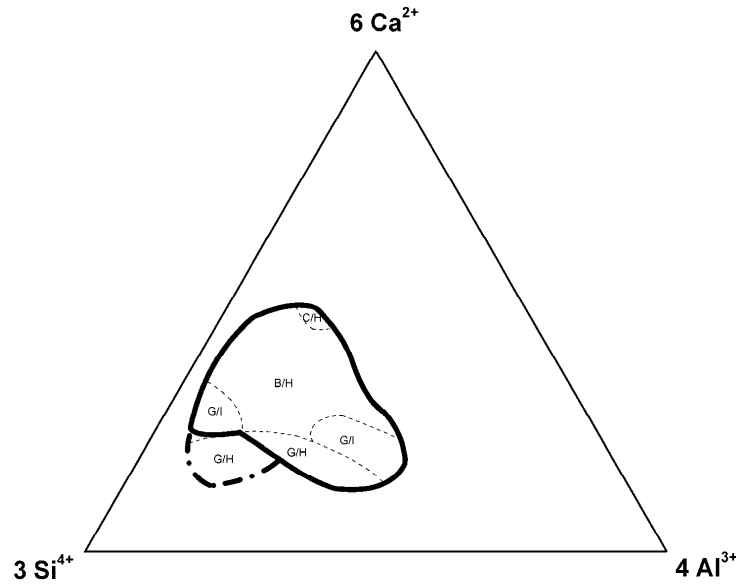


Fig. 5. Colour and homogeneity of glasses in the Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F. G = Gray, B = Black, C = Creamy, H = Homogeneous, I = Inhomogeneous.

some regions, thin slices of glass are transparent.

#### 4. GLASS STABILITY IN THE Ca-Si-Al-O-N-F SYSTEM

The effect of cation ratios and fluorine content on glass formation and crystallisation in the Ca-Si-Al-O-N-F system is shown in Table 1. It is clear that compositions which are amorphous at 5 eq.% F become crystalline when the amount of fluorine is increased. For example, for a cation composition of 28Ca:39Si:33Al eq.%, a dense glass is formed at 5 eq.% F while weight loss and precipitated  $\text{CaF}_2$  occurs when 11 eq.% F is introduced.

The previous maximum N content glass in the Ca-Si-Al-O-N system was reported as 26 eq.% N, 28Ca:56Si:16Al:74O:26N eq.% [7]. After

several attempts to find the maximum nitrogen content when 5 eq.% fluorine is introduced into the system, it was found that not more than this level of nitrogen could be incorporated. At higher nitrogen contents,  $\text{Si}_3\text{N}_4$  is precipitated which means that the network cannot dissolve more nitrogen. However, when a lower amount of fluorine (1 eq.% F) is added to the composition, nitrogen content was found to be ~40 eq.% N at the composition 28Ca:57Si:15Al:59O:40N:1F eq.% without any crystallisation occurring.

Therefore it seems that fluorine affects the dissolution of nitrogen into the melt by lowering the liquidus temperature and increasing melting range and yet does not lead to crystallisation. Introduction of higher amounts of nitrogen into the glass should result in development of glasses with excellent mechanical properties and good

Table 1. XRD analysis of Ca-Si-Al-O-N-F compositions fired at 1650 °C showing amorphous or crystalline products obtained from different fluorine content samples.

Amorphous Composition (eq.%)	Crystalline Composition (eq.%)
28Ca:39Si:33Al:75O:20N:5F	28Ca:39Si:33Al:69O:20N:11F
23Ca:47Si:30Al:75O:20N:5F	23Ca:47Si:30Al:70O:20N:10F
28Ca:45Si:27Al:75O:20N:5F	28Ca:45Si:27Al:71O:20N:9F
19Ca:57Si:24Al:75O:20N:5F	19Ca:57Si:24Al:72O:20N:8F

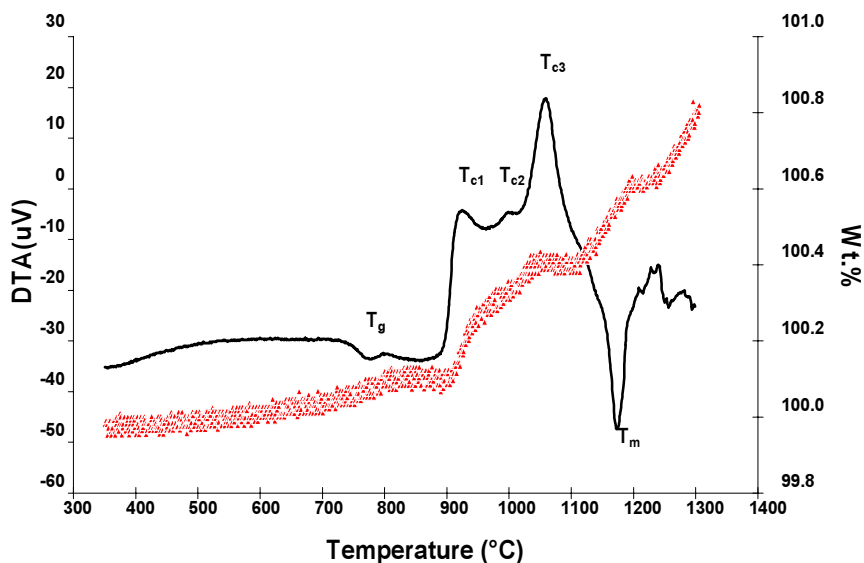


Fig. 6. DTA/TGA plot of glass 28Ca:57Si:15Al:75O:20N:5F eq.%.

chemical durability.

While oxide glasses can be formed containing up to 20 eq.% fluorine [14], it appears that the incorporation of a higher amount of fluorine is not possible in the presence of nitrogen. At 5 eq.% N, the maximum fluorine was found to be 10 eq.% F at 28Ca:57Si:15Al:85O:5N:10F eq.%, while at 10 eq.% N, the maximum was 8 eq.% F at 28Ca:48Si:24Al:82O:10N:8F eq.% and at 20 eq.% nitrogen, the maximum fluorine was 7 eq.% F at 22Ca:57Si:21Al:73O:20N:7F eq.% and 28Ca:51Si:21Al:73O:20N:7F eq.%. Therefore, it seems that by introducing more nitrogen, the amount of fluorine that can be incorporated reduces. Increasing the amount of fluorine results in  $\text{CaF}_2$  precipitation and this can be explained by the fact that N occupies the corners of Si and Al tetrahedra and, as it does not tend to bond to the glass modifier, it forces F to attach to Ca. Increasing the amount of nitrogen results in this phenomenon occurring at lower amounts of fluorine.

Nitrogen as a cross linking agent, attaches to Si atoms and reduces the possibility of  $\text{SiF}_4$  formation and, hence, stabilizes the glass composition. Fluorine has a significant effect on the solubility of nitrogen into the structure of Ca-Si-Al-O-N-F glasses and expands the glass forming region towards cation compositions that are more refractory with higher liquidus

temperatures. Therefore, it can be concluded that the two anions have a complementary effect on glass formation in the Ca-Si-Al-O-N-F system.

## 5. THERMAL ANALYSIS OF Ca-Si-Al-O-N-F GLASSES

A DTA/TGA plot of sample 28Ca:57Si: 15Al: 75O:20N:5F eq.% including glass transition ( $T_g$ ), crystallisation ( $T_c$ ) and melting temperatures ( $T_m$ ) and weight change (dashed line curve) is shown in Figure 6. Thermal analysis of Ca-Si-Al-O-N-F glasses was carried out and results are summarized in Table 2. Addition of 5 eq.% fluorine to the oxide and oxynitride glasses leads to a sudden decrease in  $T_g$  by about 94°C. This is mainly due to the disruptive role of fluorine which substitutes for bridging oxygens and facilitates the motion of the structural units in the glass. The addition of 20 eq.% nitrogen increases the  $T_g$  of oxide and oxyfluoride glasses by about 38°C.

Both ions affect the motion of structural units in the glass. Cross-linked nitrogen keeps the units more rigidly fixed and, therefore, there is an increase in the thermal energy required for segmental mobility and thus an increase in  $T_g$  [25]. Fluorine has a more marked effect in terms of its disruptive role on thermal properties than the constructive role of nitrogen.

**Table 2.** Thermal properties of Ca-Si-Al-O-N-F glasses (anions: O, O-F, O-N, O-N-F).

Composition (eq.%)	T <sub>g</sub> DTA °C	T <sub>c1</sub> °C	T <sub>c2</sub> °C	T <sub>c3</sub> °C	T <sub>m</sub> °C
28Ca:57Si:15Al:100O	810	1090	-	-	1269
28Ca:57Si:15Al:95O:5F	716	946	-	-	1206
28Ca:57Si:15Al:80O:20N	848	1043	-	-	1261
28Ca:57Si:15Al:75O:20N:5F	755	925	999	1059	1173

Both nitrogen and fluorine decrease the crystallisation temperature of oxide glass but fluorine is more effective in this regard. In oxide, oxynitride and oxyfluoride glasses, only one crystallisation peak is observed while in the oxyfluoronitride glasses, three peaks appear which are attributed to the multi-phase nature of the final crystalline glass-ceramics. The first crystallisation temperature of this glass is lower than for both oxyfluoride and oxynitride glasses. This means that a combination of these two anions effectively reduces the crystallisation temperatures of calcium aluminosilicate glasses.

Fluorine lowers the melting point of oxide and oxynitride glasses. Oxyfluoronitride glass has the lowest melting point in this series and this is mainly due to the presence of fluorine as a network disrupter.

## 6. CONCLUSIONS

1. A new generation of oxynitride glasses containing fluorine has been investigated.
2. The glass forming region in the Ca-Si-Al-O-N-F system at 20 eq.% N and 5 eq.% F is larger than the glass forming region at 20 eq.% N in the Ca-Si-Al-O-N system. Fluorine expands the range of glass formation in this oxynitride system.
3. Considerable reduction of liquidus temperatures by about 800°C at higher calcium contents shows that expansion of glass formation in the Ca-Si-Al-O-N-F system, compared with the Ca-Si-Al-O-N system, is mainly due to the effect of

fluorine.

4. Fluorine facilitates the solution of much higher amounts of nitrogen into the melt than are possible in the Ca-Si-Al-O-N system.
5. Nitrogen and fluorine play a complementary role in glass formation in Ca-Si-Al-O-N-F system.

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## REFERENCES

1. K. H. Jack, "Sialon Glasses," Proceedings of the conference on Nitrogen Ceramics. Ed. F. L. Riley, Noordhoff, Reading, MA, 1978, 257-262.
2. R. E. Leohman, *Preparation and Properties of Yttrium-Silicon-Aluminum Oxynitride Glasses*. *J. Am. Ceram. Soc.*, 1979, 62, 491.
3. R. R. Leohman, *Oxynitride Glasses*. *J. Non-Cryst. Sol.*, 1980, 42, 433.
4. R. E. Leohman, *Preparation and Properties of Oxynitride Glasses*. *J. Non-Cryst. Sol.*, 1983, 56, 123.
5. R. A. L. Drew, S. Hampshire, K. H. Jack, *Nitrogen Glasses*. *Proc. Brit. Ceram. Soc.* 1981, 31, 119.
6. R. A. L. Drew, S. Hampshire and K. H. Jack, "The Preparation and Properties of Oxynitride Glasses," Proceedings of the conference on



- Progress in Nitrogen Ceramics, Ed. F. L. Riley, 1984, 323-330.
7. S. Hampshire, R. A. L. Drew and K. H. Jack, *Oxynitride Glasses. Phys. Chem. Glass.*, 1985, 26, 182.
  8. M. Ohashi, S. Hampshire, *Formation of Ce-Si-O-N Glasses. J. Am. Ceram. Soc.*, 1991, 74, 2018.
  9. H. Y. Tu, W. Y. Sun, P. L. Wang, D. S. Yan, *Glass-Forming Regions in the Sm-Si-Al-O-N System. J. Mater. Sci. Lett.*, 1995, 14, 1118.
  10. E. Zhang, K. Liddle, D.P. Thompson, *Glass Forming Regions and Thermal Expansion of Some Ln-Si-Al-O-N Glasses (Ln= La, Nd). Brit. Ceram. Trans.* 1996, 95, 169.
  11. S. Hampshire, *Oxynitride Glasses, Their Properties and Crystallisation- a Review. J. Non-Cryst. Sol.*, 2003, 316, 64.
  12. R. E. Loehman, *Oxynitride Glasses. J. Mater. Sci. Tech.*, 1985, 26, 119.
  13. G. Leng-Ward and M. H. Lewis, "Oxynitride Glasses and Their Glass-Ceramic Derivatives," Proceedings of the conference on Glasses and Glass-Ceramics, ed. M. H. Lewis, Chapman and Hall, London, 1990, 106-155.
  14. R. Hill, D. Wood and M. Thomas, *Trimethylsilylation Analysis of the Silicate Structure of Fluoro-Alumino-Silicate Glasses and the Structure Role of Fluorine. J. Mater. Sci.*, 1999, 34, 1767.
  15. A. Stamboulis, R. G. Hill and R. V. Law, *Characterization of the Structure of Calcium Alumino-Silicate and Calcium Fluoro-Alumino-Silicate Glasses By Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR). J. Non-Cryst. Sol.*, 2004, 333, 101.
  16. T. Maeda, S. Matsuya and M. Ohta, *Effects of CaF<sub>2</sub> Addition on the Structure of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> on Glasses. J. Dent. Mater.*, 1998, 17, 104.
  17. S. Hampshire, E. Nestor, R. Flynn, J. L. Besson, T. Rouxel, H. L. Lemrcier, P. Goursat, M. Sebai, D. P. Thompson and K. Liddell, *Yttrium Oxynitride Glasses: Properties and Potential for Crystallisation to Glass-Ceramics. J. Euro. Ceram. Soc.*, 1994, 14, 261.
  18. K. T. Stanton and R. G. Hill, *Crystallisation in Apatite-Mullite Glass-Ceramics as a Function of Fluorine Content. J. Non-Cryst. Sol.*, 2005, 275, 2061.
  19. P. Jankowski and S. H. Risbud, *Formation and Characterization of Oxynitride Glasses in the Si-Ca-Al-O-N and Si-Ca-Al, B-O-N Systems. J. Mater. Sci.*, 1983, 18, 2087.
  20. W. Loewenstein and M. Loewenstein, *The Distribution of Aluminum in the Tetrahedra of Silicate and Aluminates. J. Amer. Mineral.*, 1954, 39, 92.
  21. R. G. Hill, C. Goat and D. Wood, *Thermal Analysis of a SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-CaF<sub>2</sub> Glass. J. Amer. Ceram. Soc.*, 1992, 75, 778.
  22. S. H. Risbud, R. J. Kirkpatrick, A. P. Tagliavore and B. Montez, *Solid-State NMR Evidence of 4-, 5-, and 6- Fold Aluminum Sites in Roller-Quenched SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Glasses. J. Amer. Ceram. Soc.*, 1987, 70, C10.
  23. A. Rafferty, A. Clifford, R. Hill, D. Wood, B. Samuneva and M. Dimitrova-Lukacs, *Influence of Fluorine Content in Apatite Mullite Glass Ceramics. J. Amer. Ceram. Soc.*, 2000, 83, 2833.
  24. E.M. Levin, C.R. Robbins, H. F. McMurdie, *Phase Diagram for Ceramists, American Ceramic Society, Columbus, OH, 1964, pp. 220.*
  25. M. J. Pomeroy, C. Mulcahy, S. Hampshire, *Independent Effects of Nitrogen Substitution for Oxygen and Yttrium Substitution for Magnesium on the Properties of Mg-Y-Si-Al-O-N Glasses. J. Am. Ceram. Soc.*, 2003, 86, 458.